

Anomalous metallicity and electronic phase separation in the CsC_{60} polymerized fulleride

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Abstract

^{133}Cs and ^{13}C -NMR have been used to study the electronic properties of the polymerized phase of CsC_{60} at ambient and under hydrostatic pressure. The salient result of this study is the finding of fluctuations in the local field at ^{133}Cs site which are independent of the applied pressure and due to thermally activated changes in the local electronic environment of ^{133}Cs nuclei. We establish that the phase separation between magnetic and nonmagnetic domains observed in the low temperature state at ambient pressure is the result of a slowing down of these fluctuations likely related to polaronic charge excitations on the polymers.

I. INTRODUCTION

When the face centered cubic (f.c.c) phase of A_1C_{60} ($A=K, Rb, Cs$) compounds is slowly cooled from 400K, one-dimensional polymerization of C_{60} molecules spontaneously occurs along the (110) cubic direction and leads to an orthorhombic phase [1]. A drastic change in the electronic properties is observed at the structural transition [2,3]. Indeed, the f.c.c. phase was shown to be a Mott insulator [2,3], whereas in the orthorhombic phase a plasma frequency was measured in optical experiments [4]. However, the density of carriers is likely to be rather low or their effective mass very large since the plasma frequency is equal to 0.1eV in KC_{60} polymer and even lower for RbC_{60} and CsC_{60} [4]. In addition, the low frequency conductivity of both RbC_{60} and CsC_{60} decreases smoothly over a broad temperature range, being at variance with KC_{60} which remains conducting down to 4.2K [4]. Furthermore, the temperature dependence of the ^{13}C spin-lattice relaxation rate shows that strong magnetic fluctuations are present up to room temperature in RbC_{60} and CsC_{60} [5] and the sharp decrease of the uniform static susceptibility (measured from EPR line intensity) below 50K for RbC_{60} and 40K for CsC_{60} [4], suggests that both compounds undergo magnetic transitions at these respective temperatures. The occurrence of spin ordering is also evident from NMR experiments [5,6]: the slowing down of magnetic fluctuations gives rise to a divergent relaxation rate below 40K. However, the nature of the spin order is less obvious. On one hand, EPR experiments [7,8] suggest the onset of a spin density wave ground state as a result of a possible one-dimensional (1D) character of the band structure. On the other hand, μ SR studies [9,10] show a gradual transition towards a highly disordered magnetic phase and do not rule out the possibility of a random spin freezing below 40K.

In a recent NMR work [11], we have shown that some of the ^{133}Cs sites remain unaffected by the onset of the spin-ordering in the low temperature state, magnetic and nonmagnetic domains being spatially distributed. At the temperature of 13.8K the occurrence of a charge redistribution and a concomitant decrease of the local electronic susceptibility inside these nonmagnetic domains have been observed [11]. In agreement with this latter result, detailed

analysis of the EPR linewidth at ambient pressure also suggest that two distinct magnetic environments coexist in the low temperature state of RbC_{60} and CsC_{60} polymers [12,13] and insofar as a charge redistribution occurs in the nonmagnetic domains at 13.8K [11], the spontaneous thermal contraction recently observed at 14K by X-Ray diffraction in CsC_{60} [14] strongly supports the fact that these inhomogeneities are intrinsic.

In this manuscript, we give experimental evidence showing that the “conducting” state of the CsC_{60} polymerized phase cannot be understood within the framework of an electronic band conductor as claimed earlier [3–5,7,8,18] . We first report the temperature dependence of the spin lattice relaxation rate $(T_1)^{-1}$ for both ^{13}C and ^{133}Cs nuclei at different pressures up to 9 kbar, indicating that in the temperature domain above 80K two different mechanisms govern the relaxation of ^{13}C and ^{133}Cs nuclei respectively. As far as ^{133}Cs is concerned, $^{133}(T_1)^{-1}$ decreases linearly down to about 80K though remaining pressure independent up to 9kbar. This behavior is in sharp contrast with the ^{13}C nuclei for which $^{13}(T_1)^{-1}$ strongly decreases under pressure up to 9kbar while remaining almost temperature independent. The difference between ^{133}Cs and ^{13}C nuclei exists *independently* of the nature of the ground state of the system. More insight into these peculiar properties is then obtained using quadrupolar echo experiments performed on the ^{133}Cs nucleus which enable us to analyze with great accuracy the temperature dependence of the NMR spectrum at 1bar. We show that the NMR spectrum of the two phases (magnetic and nonmagnetic) is motional narrowed above 100K because of the fast motion of the local environment around the ^{133}Cs sites. The evolution of the lineshape with temperature reveals that the static coexistence of two different ^{133}Cs sites below 15K arises from a gradual freezing of these fluctuations in the local environment.

II. EXPERIMENTAL DETAILS

The measurements have been conducted on two powdered samples with entirely consistent results, one of them (10%) ^{13}C enriched. The pressure set up is a homemade double-

stage copper-beryllium cell using fluor-inert as the pressure medium. This enables us to correct for each temperature the loss of pressure within the sample chamber due to the gradual freezing of the fluor-inert.

The spin-lattice relaxation were measured by monitoring the recovery of the magnetization after saturation with a series of $\pi/2$ pulses. The recovery curve is exponential for ^{133}Cs and ^{13}C [15] at room temperature. At ambient pressure, the recovery curve gradually becomes bi-exponential for both nuclei below 40K. A large distribution of short relaxation rates is observed giving raise to a recovery curve of the following shape $1 - e^{(-t/T_1)^\beta}$ with a value of β of the order of 0.5 at the lowest temperature investigated i.e 4K. At 5kbar the recovery curve is for ^{133}Cs exponential down to 4K. Not so for ^{13}C since a nonexponential recovery is observed below 20K. Different fit procedures did not help us to determine without ambiguity the shape of the recovery but no significant change were observed on the qualitative temperature dependence of $^{13}(T_1)^{-1}$. The relaxation rates $^{13}(T_1)^{-1}$ shown on Fig.1b at 5kbar are therefore deduced below 20K from a fit of the recovery curve assuming it to be exponential as above 20K. At 9kbar, the recovery curve is exponential for ^{133}Cs and ^{13}C in the all temperature range investigated.

Finally we should point out that despite the presence of a static quadrupole splitting [16] for the NMR line of ^{133}Cs in the orthorhombic phase, the smallness of the quadrupole frequency which is of the order of 5kHz enables us to saturate all the transitions at once. Therefore the nuclear levels are initially equally populated establishing a well-defined spin temperature (equal to infinite). In that case no deviation from an exponential behavior is expected for the relaxation of the magnetization [17] which perfect exponential recovery at room temperature is a proof of the homogeneity of the samples.

III. ^{13}C AND ^{133}CS -NMR UNDER PRESSURE

We report on Fig.1a and Fig.1b the temperature dependence of the relaxation rate for ^{133}Cs and ^{13}C nuclei at ambient pressure, 5kbar and 9kbar. The large enhancement of

$^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ below 40K is due to a slowing down of magnetic fluctuations which is completely suppressed at 5kbar. At this pressure, both $^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ decrease exponentially below 20K revealing the opening of a spin-gap at $T_C \approx 20K$, the ground state being homogeneous and nonmagnetic. The effect of an applied pressure on this long range order has been carefully investigated by ^{133}Cs -NMR. The temperature dependence of $^{133}(TT_1)^{-1}$ at 5, 5.5, 5.7 and 9kbar is shown in Fig.2. The well-defined instability at 5kbar gives rise to a sharp peak on $^{133}(TT_1)^{-1}$ at T_C . Quite remarkably, a slight increase of the applied pressure strongly reduces the amplitude of the spin-gap, without any significant change in T_C itself (as given by the position of the $^{133}(TT_1)^{-1}$ peak, see on Fig.2). However, a smooth decrease of the temperature T_{Mag} at which the slowing down of magnetic fluctuations occurs has been observed by EPR experiments under pressure up to 4kbar [22]. This fact is also evident from the temperature dependence of the linewidth of the ^{133}Cs NMR line shown at different pressures on Fig.3. Thus, as the pressure increases T_{Mag} drops continuously along a transition line which does not exist for the case of the spin-singlet ground state. Henceforth we can infer that the sharp suppression of the spin-gap below 20K which in turn gives rise to a metallic state, is not due to continuous changes in the magnitude of the electronic interactions but may reflect some structural changes above 5kbar as suggested by DC conductivity measurements performed under pressure [19,20].

Another striking feature in the response of the polymerized phase CsC_{60} to high pressure appears at glance in Fig.1a and Fig.1b. Indeed, a clear distinction has to be made between the two temperature domains 4.2-80K and 80K-300K. Below 80K, $^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ exhibit a similar pressure and temperature dependence. This is, however, no longer true above 80K, where $^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ behave in complete different ways. In particular, we can see in Fig.1a that above 80K, $^{133}(T_1)^{-1}$ shows no pressure dependence up to 9kbar unlike $^{13}(T_1)^{-1}$, which is shown on Fig.1b. Within the first five kilobars, the relaxation of ^{13}C nuclei is strongly affected by pressure in two manners: (i) an overall depression is observed under pressure following the depression of the uniform spin susceptibility (χ) measured by EPR [22] which drops at a rate of about 10% per kbar, (ii) a weakly temperature dependent

contribution to $^{13}(T_1)^{-1}$ (20% decrease from 300 to 40K) is suppressed at 5 kbar.

Broadly speaking, the spin-lattice relaxation rate for a given nuclei and the static electronic spin susceptibility are linked together by the following relation : $(T_1T)^{-1} \propto \sum_q |A(\vec{q})|^2 \chi_{\perp}''(\vec{q})$ where $A(\vec{q}) = \sum_i A_i e^{i\vec{q} \cdot \vec{r}_i}$ is the form factor of the hyperfine interaction between a given nuclei and the electronic spins located at the neighboring sites. Unlike ^{133}Cs which environment is octahedral, there is no particular symmetry for ^{13}C sites. If both nuclei are coupled to the same electronic spins then, that $^{13}(T_1)^{-1}$ and $^{133}(T_1)^{-1}$ display a different pressure and temperature dependence above 80K, might be attributed to the presence of a spatially dependent electronic spin susceptibility which dominates the relaxation of ^{13}C nuclei. However, as previously shown for RbC_{60} [6], the decrease of $^{13}(T_1)^{-1}$ follows the decrease of the uniform spin susceptibility deduced from EPR [22] within at least the first five kilobars. This reveals that in the low pressure regime, the dominant contribution to the relaxation of ^{13}C above 80K is due to enhanced magnetic fluctuations at the wave vector $\vec{q} = 0$ and therefore, the differences described above between ^{13}C and ^{133}Cs cannot be ascribed to the form factor of the alkali site in the polymerized phase.

As it is, one can draw the following conclusions. First, the absence of pressure dependence observed for $^{133}(T_1)^{-1}$ above 80K shows that the dominant contribution to the fluctuating field at ^{133}Cs site in this temperature range is unrelated to the electronic spins involved in the relaxation of ^{13}C nuclei. Secondly, the fact that above 80K, $^{13}(T_1)^{-1}$ is weakly temperature dependent at ambient pressure and constant at 5kbar suggests that the electronic spins are localized. This latter conclusion is in agreement with the calculated band structure of the polymer $(\text{C}_{60}^-)^n$ [21] which displays a dispersionless 1D half-filled band at the Fermi level but in apparent contradiction with transport measurements [19,20] performed in the similar compound RbC_{60} .

One can therefore conclude that a model based on a single electron specie is inadequate for describing the electronic properties of the polymerized phases RbC_{60} and CsC_{60} .

In a previous work [11], we have shown that the use of quadrupolar spin echoes of ^{133}Cs nuclei enables to reveal the presence of nonmagnetic domains within a magnetic background.

However, whether this inhomogeneous state results from the existence of static structural defects along the chains or is purely electronically driven e.g. as proposed for underdoped cuprates [23] and spin-ladders compounds [24], remained an open question. In what follows, we address this problem again with the aid of quadrupolar spin echoes in order to determine how the inhomogeneous state at low temperature arises from the high temperature one.

IV. ^{133}Cs -NMR AT AMBIENT PRESSURE

In a similar way than in the reference [11], the spin echoes of ^{133}Cs have been obtained after a $(\pi/2 - \tau - \pi/8)$ in-phase RF pulse sequence [25], maintaining fixed the echo delay τ at $40\mu\text{s}$. Half of the spin-echo at 3τ is then Fourier transformed. This procedure gives rise to a spectrum containing two lines $5/2 \rightarrow 3/2$ and $-3/2 \rightarrow -5/2$ split by an amount $4\nu_Q$, where ν_Q is the quadrupole frequency of ^{133}Cs nuclei in the polymerized phase [11,26]. The evolution of the ^{133}Cs spectrum is displayed on Fig.4 at different temperatures between 100 and 4.2K. The expected doublet spectrum corresponding to a single ^{133}Cs site is observed at 100K, but as T approaches 40K, the shape becomes asymmetric and a fine structure gradually develops. At 25K, the coexistence of two different ^{133}Cs sites is evident in Fig.4, with a frequency difference in the local field of the order of $4\nu_Q$. This means therefore that two distinct magnetic environments are spatially distributed at this temperature. As the temperature is further lowered, the situation with a single quadrupolar split is recovered and thus only one ^{133}Cs site contributes to the spin echo signal below 15K. The amplitude of the spin echo refocused at 3τ is proportional to $e^{-3\tau\gamma\Delta H(T)}$ where $\Delta H(T)$ is the width of the local field distribution due to the static electronic moments at a given temperature T . Considering two distinct populations of ^{133}Cs nuclei below 30K, N_m and N_{nm} which are coupled to the local field inhomogeneity $\Delta H(T)$ and located inside the nonmagnetic domains respectively, the total number of ^{133}Cs sites contributing to the spin echo signal at 3τ can be expressed as: $N(T) = N_m/(1 + (3\tau\gamma\Delta H(T))^2) + N_{nm}$. If the condition $3\tau\gamma\Delta H(T) \gg 1$ is fulfilled, only a fraction N_{nm} of the nuclei contribute to a spin echo at 3τ since this exper-

iment selects those Cs sites which are entirely decoupled from the onset of local magnetism. Let $I(T)$ be the integrated intensity of the Fourier transform performed on this spin echo. The temperature dependence of $N(T)$ (equal to $I(T).T$) is reported on Fig.5. We observe that a majority of the ^{133}Cs nuclei is gradually wiped out of the signal below 40K. A minimal value for N_{nm} is reached at 15K and amounts to about 10% of the total number of nuclei at 40K. However, the estimated ratio between the two phases from the ^{13}C spectrum suggests that approximately half of the ^{13}C sites do not see the magnetic moment distribution in the low temperature state [5]. We may solve this puzzle by considering that the ^{13}C spins probe the very local properties within each C_{60} chains carrying the electronic spins whereas only ^{133}Cs sites far from any magnetic domain will contribute to the echo signal refocused at 3τ . This would mean that the boundary surface is large compare to the domains size suggesting that the phase separation sets on a microscopic scale.

To gain insight into the driving force of this process more attention must be paid to what happens above the spin ordering temperature. In particular, we see on Fig.4 that the splitting of the ^{133}Cs spectrum displays a fine structure near 40K although the NMR spectrum corresponding to two ^{133}Cs sites is not yet resolved. This can be understood if we assume that the local field of a ^{133}Cs nucleus jumps randomly from one value to the other in the “conducting” state. Indeed, using only the difference between the resonance frequencies $\delta\omega$ and the hopping time τ_h , we can propose the following scenario. At high temperature, $\delta\omega\tau_h \ll 1$ and the spectrum is motional narrowed, which means that only one doublet is visible. When the temperature is lowered, the jump frequency ($1/\tau_h$) decreases and the condition $\delta\omega\tau_h \approx 1$ becomes fulfilled with a fine structure developing in the NMR spectrum. Finally, when $\delta\omega\tau_h \gg 1$, the quadrupolar splitting of the two sites are well resolved, *i.e.* one for ^{133}Cs sites in the magnetic domains and the other for ^{133}Cs sites in the nonmagnetic ones. We simulate each of the three cases and our simulations at fixed $\delta\omega$ are shown in Fig.6 for different correlation times τ_h and superimposed (dotted line) on the experimental spectra on Fig.4. Clearly, the calculated spectra bear a strong resemblance with the experimental ones displayed on Fig.3 between 100 and 30K. We can thus infer the existence of a

thermally activated change in the local environment of ^{133}Cs sites which may become the dominant contribution to $^{133}(T_1)^{-1}$ when the frequency $1/\tau_h$ is of the order of the Larmor frequency (43 MHz) of the ^{133}Cs nuclei. Therefore, from the results exposed in this section we can conclude to the existence of another degree of freedom aside from the fluctuations of the electronic spins located on the C_{60} molecules, and possibly related to spontaneous local structural changes in the polymerized phase.

V. DISCUSSION

As emphasized above, one of the difficulty aroused by our work is to bring together the conducting nature of the polymerized phase established by optical and transport measurements [4,19,20] with the pressure and temperature dependence of $^{133}(T_1)^{-1}$ which strongly suggest that electrons are localized. It therefore turns out natural to question ourselves about the possible relationship between the local structural change around ^{133}Cs nuclei and the presence of charge degrees of freedom like polarons in the polymerized phase. On the basis of the above NMR results and anticipating results described further on, we suppose that the mobility of a charge carrier in the polymerized phase mainly depends upon the occurrence of a local structural distortion in its vicinity. From a point of view which is somewhat naive, one may consider that at thermal equilibrium, the charge carriers diffuse through the lattice under the action of a random force $F(t)$ which takes on only two discrete values $\pm f_0$. For our particular purpose, the relevant physical quantity to be consider is the spectral density $F(\omega)$ defined as the Fourier transform of the correlation function $\langle F(t)F(t+\tau) \rangle$, the brackets indicating an ensemble average. In our case, $\langle F(t)F(t+\tau) \rangle$ can be assumed to be of the form [28]: $f_0^2 e^{-|t|/\tau_h}$, which leads to the following spectral density : $F(\omega) = \tau_h/(1 + (\omega\tau_h)^2)$. Because any excited state of the charge carriers is to relax due to the random force $F(t)$, the spectral density $F(\omega)$ will lead to a strong frequency dependence in the response function of the carriers to external oscillating fields. It is therefore of a great interest to focus on AC resistivity measurements [20] performed at ambient pressure in both KC_{60} and RbC_{60} .

For KC_{60} which does not exhibit a slowing down of spin fluctuations, AC and DC resistivities display a similar temperature dependence. This is however not true for RbC_{60} since a frequency dependent peak is clearly observed on AC resistivity. The peak shifts from 35K at 1.1kHz down to 25K at 43Hz, the order of magnitude of these frequencies being in good agreement with the value we deduced from our simulate spectra in the same temperature range for CsC_{60} (c.f.Fig.6). The fact that the electronic properties of RbC_{60} and CsC_{60} display similar electronic and structural features as opposed to KC_{60} allows us to extrapolate the results obtained by Zhou *et al* for RbC_{60} to the case of CsC_{60} . Thus experiments show that in the two polymerized phases RbC_{60} and CsC_{60} , the dissipation reaches a maximum when the hopping frequency of the local environment of the alkali ion becomes equal to the AC frequency. Such a coincidence can be hardly fortuitous and suggests that the mobility of the charge carriers in the polymerized phase is strongly coupled to the environment of the alkali ion. In this context, it is worthwhile to mention that polaron-like distortions such as $\text{C}_{60}^{-1-x} - \text{C}_{60}^{-1+x}$ have been predicted to be energetically favorable in the charged polymer $(\text{C}_{60}^-)^n$ which exhibits a tendency to undergo a charge density wave transition [27]. In that particular case, the conduction mechanism would be due to an intramolecular property of the polymer itself and that would drastically change our expectations regarding the pressure effect on the electronic properties of the polymerized phase. However, on the sole basis of the NMR experiment above described we cannot address the microscopic mechanism at the origin of the spontaneous formation of polarons in the polymerized phase.

In the light of the above considerations, it is interesting to shortly reconsider the pressure effect on the spin-lattice relaxation rate $^{13}(T_1)^{-1}$ of ^{13}C nuclei in the low pressure regime. As mentioned above, $^{13}(T_1)^{-1}$ shows at room temperature a similar pressure decrease than the electronic spin susceptibility deduced from EPR [6] which suggests that magnetic fluctuations at the wave vector $\vec{q} = 0$ dominate $^{13}(T_1)^{-1}$ at ambient pressure. One possible explanation for the origin of these enhanced uniform fluctuations might be that polarons acting as local defects, induce disorder in the AF exchange coupling J along the chain leading to the formation of spin clusters [29]. It was indeed shown theoretically [29] that the

low energy magnetic fluctuations (i.e when $T \ll J$) of a disordered AF spins chain are merely governed by clusters with an odd number of spins, each one acting as a nearly free localized (1/2) spin. In such a case the *reversible* suppression at 5kbar of a weak temperature dependent term in $^{13}(T_1)^{-1}$ could be ascribed to the suppression with applied pressure of disorder in the magnetic coupling along the chain which presence would be henceforth closely related to the slowing down of spin fluctuations in the low temperature state. Much more experimental inputs are however required to go beyond this statement.

As it is, the phase separation occurring in the low temperature state at ambient pressure appears to be the logical outcome of the twofold nature of the polymerized phase CsC₆₀ that is : mobile polarons spontaneously form aside from localized electrons and compete with a 3D magnetic order imposed by the transverse dipolar coupling between the chains. Note that the presence of nonmagnetic domains is in itself a strong hint that polarons are not randomly spatially distributed within the magnetic background but may form collective structures developing a long range order below 14K as suggested by NMR [11] and X-ray experiments [14].

VI. CONCLUSION

The work described in this manuscript deals with the electronic properties of the polymerized phase CsC₆₀ extensively studied by NMR of ^{13}C and ^{133}Cs nuclei. The salient result is that the electronic properties of the polymerized phase CsC₆₀ involve two degrees of freedom : one related to localized spins, the other related to mobile charges which mobility is strongly entangled to the local environment of the Cs ion. The polymerized phase CsC₆₀ is therefore dynamically inhomogeneous and as shown by NMR under pressure, this feature persists up to 9kbar.

At ambient pressure static inhomogeneities gradually develop below 40K concomitantly with a slowing down of spin fluctuations. At 5kbar, the polymerized phase CsC₆₀ undergoes a nonmagnetic transition at T_c equal to 20K. The ground state is homogeneous and a spin gap

opened below 20K. Finally, a dramatic decrease of the amplitude of the spin gap is observed above 5kbar without any significant decrease of T_c . The presence of magnetism therefore appears to be closely related to the occurrence of static inhomogeneities. How does the applied pressure suppress these inhomogeneities and stabilize a homogeneous nonmagnetic ground state? That cannot be addressed by the present work but remains an important issue to be solved.

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REFERENCES

- * Present address: Condensed Matter and Thermal Physics, MST-10 MS K764, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.
- [1] P. W Stephens *et al*, Nature **370**, 636 (1994).
- [2] R. Tycko, G. Dabbagh, D. W. Murphy, Q. Zhu, and J. E. Fischer, Phys. Rev. B **48**, 9097 (1993).
- [3] O. Chauvet *et al.*, Phys. Rev. Lett. **72**, 2721 (1990).
- [4] F. Bommeli *et al.*, Phys. Rev. B **51**, 14794 (1995).
- [5] V. Brouet, H. Alloul, Y. Yoshinari, and L. Forró, Phys. Rev. Lett. **76**, 3638 (1996).
- [6] P. Auban-Senzier, D. Jérôme, F. Rachdi, G. Baumgartner, and L. Forró, J. Phys.I France **6**, 1 (1996).
- [7] A. Jánossy *et al.*, Phys. Rev. Lett. **79**, 2718 (1997).
- [8] M. Bennati, R. G. Griffin, S. Knorr, A. Grupp, and M. Mehring, Phys. Rev. B **58**, 15603 (1998).
- [9] W. A. MacFarlane, R. F. Kiefl, S. Dunsiger, J. E. Sonier, and J. E. Fischer, Phys. Rev. B **52**, 6695 (1995).
- [10] Y. J Uemura *et al.*, Phys. Rev. B **52**, 6691 (1995).
- [11] B. Simovič, D. Jérôme, F. Rachdi, G. Baumgartner, and L. Forró, Phys. Rev. Lett. **82**, 2298 (1999).
- [12] V.A. Atsarkin,V.V. Demidov and G.A. Vasneva, Phys. Rev. B **56**, 9448 (1997).
- [13] C. Coulon, J. Duval, C. Lavergne, A.L. Barra, and A. Pénicaud, J. Phys.IV France **10**, 205 (2000).
- [14] S. Rouzière, S. Margadonna, K. Prassides, and A.N. Fitch, cond-mat/0002419

- [15] We can always fit the recovery curve with the expression $M(t) = M_{eq}(1 - e^{(-t/T_1)^\beta})$, M_{eq} being the equilibrium magnetization and β a dimensionless coefficient comprised between 0.5 and 1. At room temperature and at any pressure investigated β is equal to 1 for ^{133}Cs whereas a substantial deviation from an exponential recovery is observed i.e $\beta \approx 0.72$ for ^{13}C . Because of the possible presence of a small amount of pure amorphous C_{60} , such deviation might be extrinsic. Therefore, we talk about "exponential recovery" for ^{13}C as opposed to the dramatic changes in the recovery curve observed at low temperature and which occurrence is unambiguously related to some intrinsic properties of the polymerized phase.
- [16] The presence of a quadrupole splitting does not imply a quadrupole relaxation but is consequent to the noncubic symmetry of the local environment of ^{133}Cs site. For a cubic symmetry the three components of the electric field gradient are strictly equal to zero which implies no quadrupole splitting. However, any fluctuations leading to a substantial deviation from the cubic symmetry may lead to a quadrupole relaxation depending upon the magnitude of the quadrupolar coupling compare to others. For the particular case of ^{133}Cs , the possibility of a quadrupole contribution in the relaxation of the magnetization can be easily ruled out because of the remarkably small value of its quadrupole moment.
- [17] A detail analysis of the magnetization recovery for nuclear spin $I > 1/2$ can be found in the following reference : A. Suter, M. Mali , J. Roos, and D. Brinkmann, J. Phys. Condens. Matter **10**, 5977 (1998)
- [18] S.C. Erwin, G.V. Krishna, and E.J. Mele, Phys. Rev. B **51**, 7345 (1995).
- [19] K. Khazeni, V. H. Crespi, J. Hone, A. Zettl, and M. L. Cohen, Phys. Rev. B **56**, 6627 (1997).
- [20] W.Y. Zhou,S.S. Xie,L. Lu,E.S. Liu, and Z. Peng, Journal of Physics and Chemistry of Solids **61**, 1159 (2000).

- [21] S. Stafström, M. Boman, and J. Fagerström, *Europhysics. Lett.* **30**, 295 (1995).
- [22] L. Forró *et al.*, in *Progress in Fullerene Research*, edited by H. Kuzmany *et al* (World Scientific, Singapore 1996)
- [23] O. Zachar, S.A. Kivelson, and V. J. Emery, *Phys. Rev. B* **57**, 1422 (1998).
- [24] S.R. White, and D.J. Scalapino, *Phys. Rev. B* **55**, 14701 (1997).
- [25] For a given nuclei, the amplitude of the spin echoes strongly depends upon the angle of the rotation applied by the second pulse to the magnetization as well as the relative phase between the two pulses. For the in-phase pulse sequence $(\pi/2 - \tau - \pi/8)$ applied on ^{133}Cs nuclei, the calculated [26] amplitude of the spin echo is maximal at 3τ and strongly reduced at $5\tau/2$ and 4τ .
- [26] B. Simovič, Thesis, Université Paris-Sud, Orsay (1999).
- [27] M. Springborg, *Phys. Rev. B* **52**, 2935 (1995).
- [28] C.P.Slichter, Appendix C in *Principles of Magnetic Resonance*, Third edition, Springer-Verlag (1990).
- [29] G. Theodorou, *Phys. Rev. B* **16**, 2264 (1977).

FIGURES

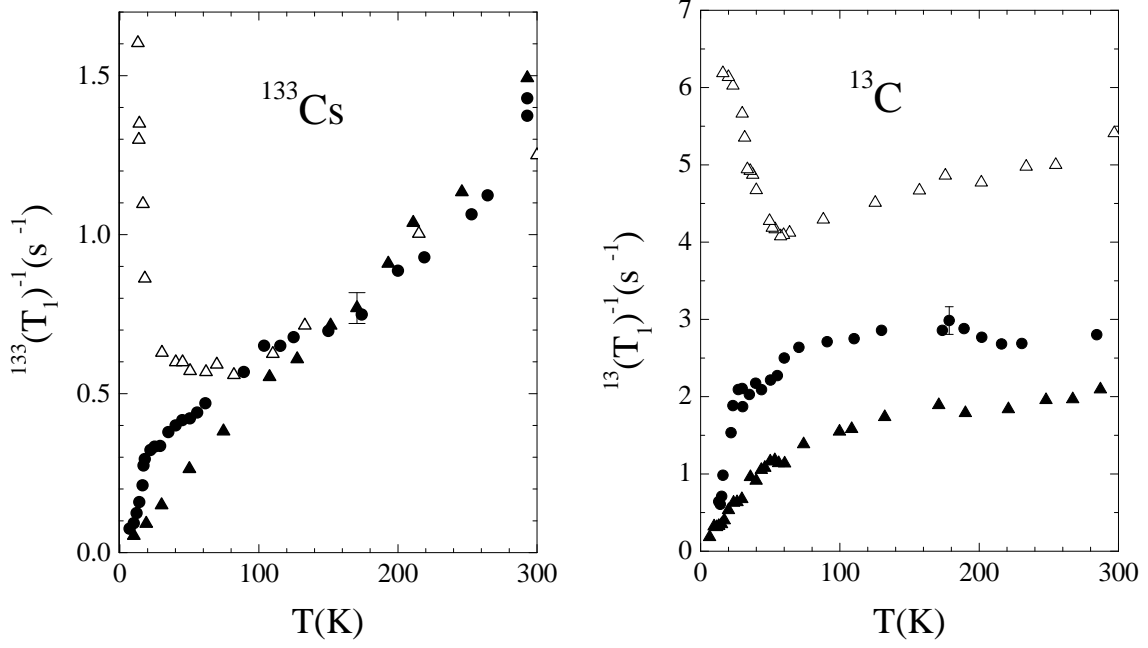


FIG. 1. Temperature dependence of T_1^{-1} for (a) ^{133}Cs (at 8 Tesla) and (b) ^{13}C (at 9 Tesla), at 1bar (empty triangles), 5kbar (black circles) and 9kbar (black triangles). At 1bar and below 40K, the magnetization recovery curves are bi-exponential for both ^{133}Cs and ^{13}C but only the rapid component is reported versus temperature.

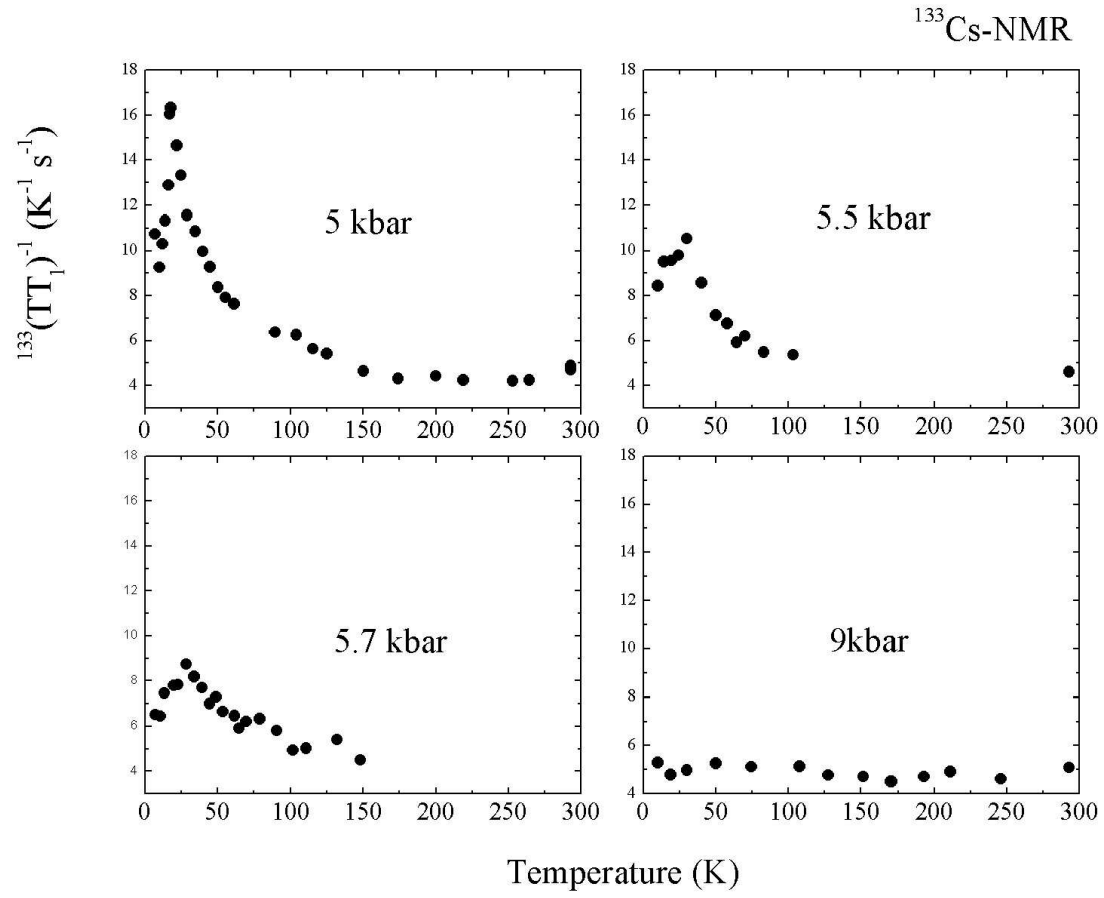


FIG. 2. Temperature dependence of $^{133}(\text{TT}_1)^{-1}$ at 5kbar, 5.5kbar, 5.7 and 9kbar.

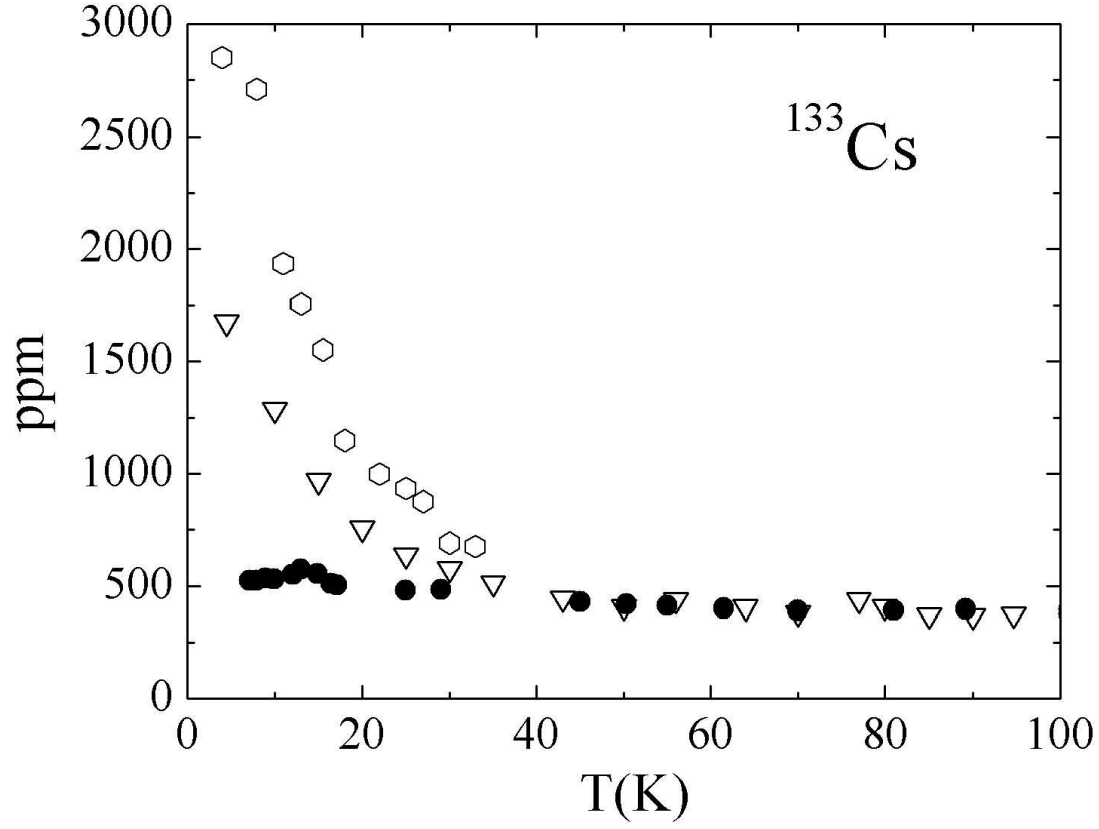


FIG. 3. Temperature dependence of the linewidth of the ^{133}Cs -NMR line at 1bar from ref [5] (empty hexagons), at 3kbar (present study, empty triangles) and at 5kbar (present study, full circles).

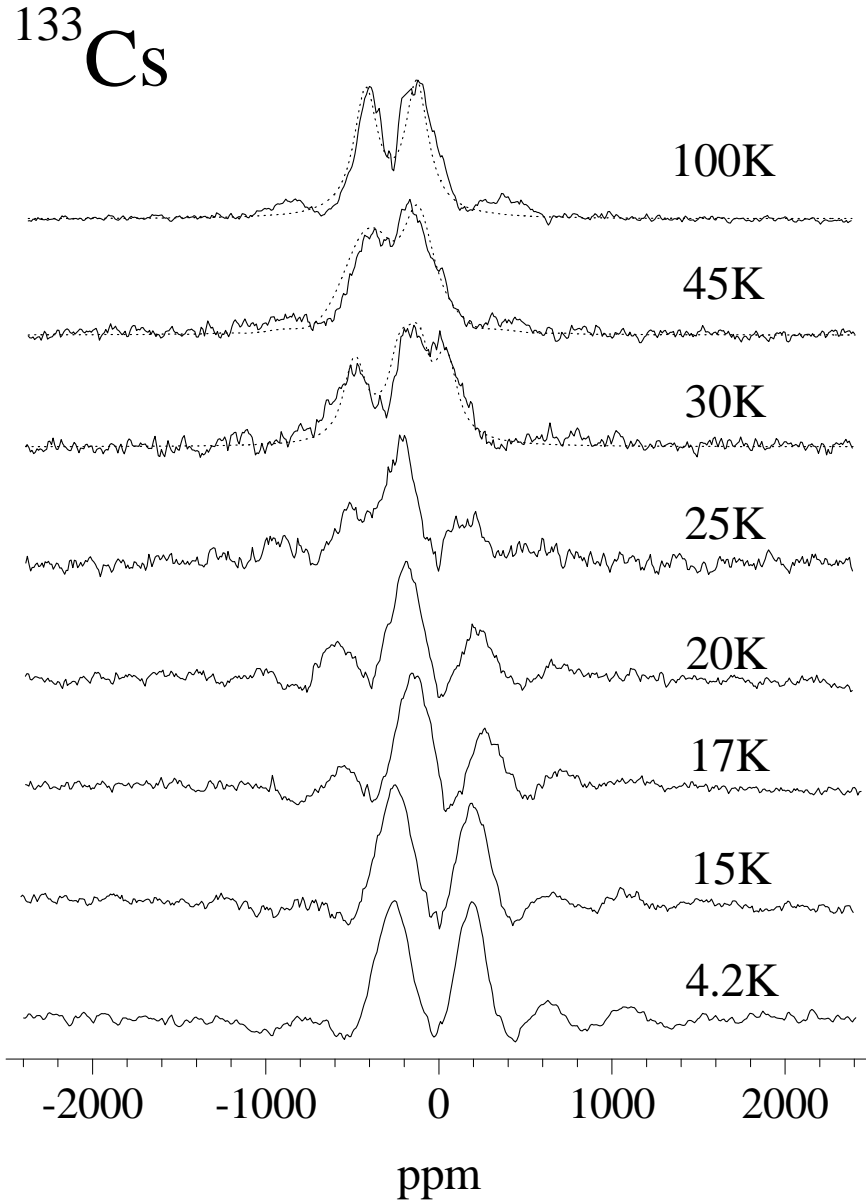


FIG. 4. Evolution of the lineshape of the ^{133}Cs quadrupolar normalized splitting from 100K down to 4.2K. Because we take the Fourier transform of half of the spin echo at 3τ , the other spin echoes induce distortion of the base line.

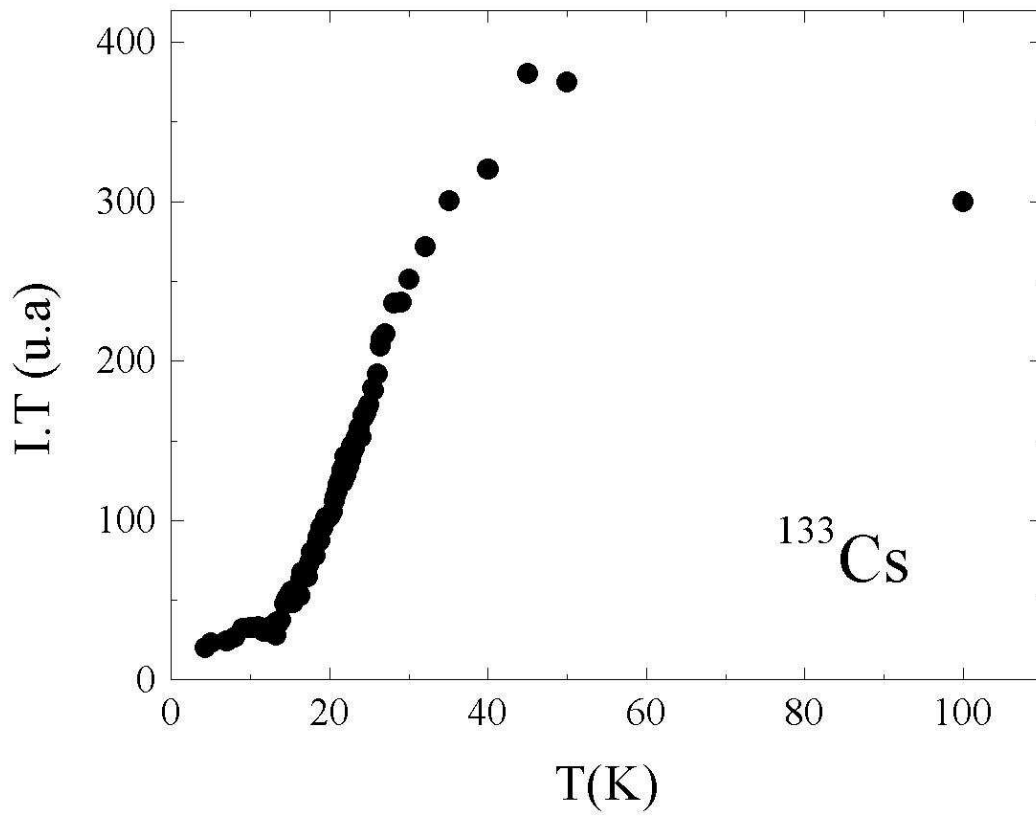


FIG. 5. Temperature dependence of $N(T) = I(T) \cdot T$ where $I(T)$ is the integrated intensity of the Fourier transform of half of the spin echo refocused at 3τ .

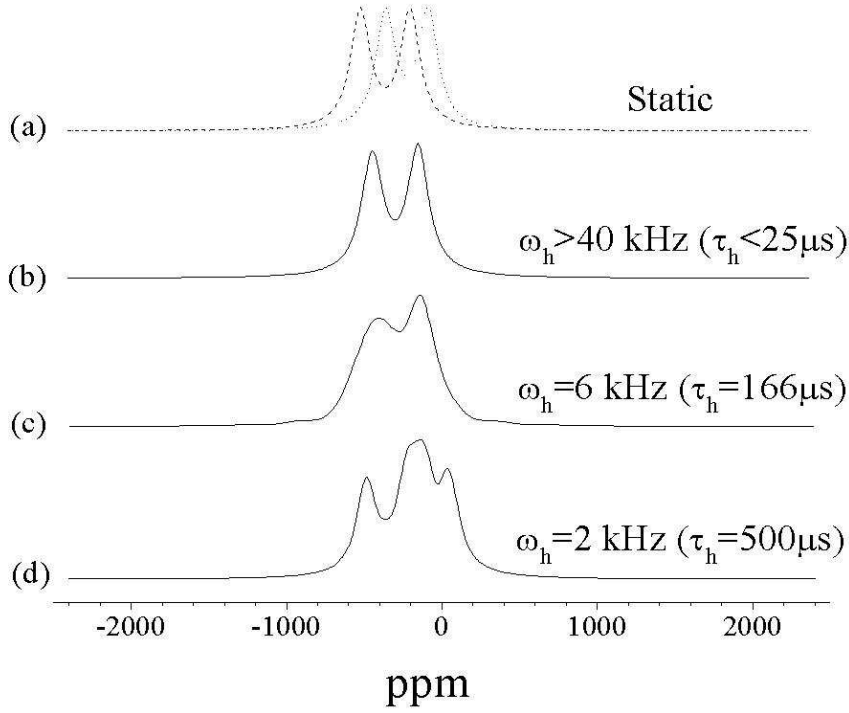


FIG. 6. Simulation of the shape of the ^{133}Cs quadrupolar spectrum. (a) In the static case : for each of the two configurations, both the quadrupole frequency ν_Q and the frequency shift K compare to the Larmor frequency are determined from the spectrum at 100K *i.e.* in the fast motion limit. This gives the respective values : $\nu_Q=4.17\text{kHz}$ and $K=-350\text{ppm}$ (dashed line), $\nu_Q=3.57\text{kHz}$, $K=-209\text{ppm}$ (dotted line). (b) In the fast motion limit : $\delta\omega\tau_h \ll 1$. (c) In the slow motion limit : $\delta\omega\tau_h \approx 1$. (d) For a *quasistatic* distribution : $\delta\omega\tau_h \gg 1$.